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# Verfahren zur Herstellung von tri- und tetravalenten Gläsern.

Die Erfindung bezieht sich auf ein Verfahren zur Herstellung von tri- und tetravalenten Gläsern, die Nitride und Carbide der Metalle der 4. bis 6. Nebengruppe des Periodensystems enthalten.

Bekannte Gläser sind das monovalente Fluoberyllatglas und die divalenten oxydischen Gläser, so Borat-, Silikat-, Germaniat-, Phosphat- und Arsenatgläser, als Seltenheit Sulfidgläser. Das einfach zusammengesetzte Natron-Kalk-Glas, das die Zusammensetzung  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$  hat, ist das "Normalglas". Durch mehr oder weniger weitgehende Änderungen in der Zusammensetzung erhält man außer den Normalgläsern noch Hunderte von Spezialgläsern mit jeweils neuen Eigenschaften. Gegenüber dem monovalenten Fluoberyllatglas sind die oxydischen, divalenten Gläser in ihren Lichtbrechungs- und Härteeigenschaften gesteigert.

Von größtem technischen Interesse wäre es nun, eine nochmalige Steigerung der Eigenschaften durch den Übergang auf tri- oder gar tetravalente Gläser zu erreichen. Das ist die Aufgabe der vorliegenden Erfindung.

Gelöst wird diese Aufgabe dadurch, daß den Schmelzen monovalenter und divalenter Gläser, vorzugsweise den Schmelzen der divalenten Gläser, metallisches Titan in Pulverform zugeführt wird, das mit den in den Schmelzen enthaltenen Gasen wie Stickstoff  $\text{N}_2$ , Kohlenmonoxid  $\text{CO}$ , Kohlendioxid und anderen unter Bildung von Nitriden und Carbiden reagiert. Es bilden sich solche Reaktionsprodukte, die von der Schmelze gelöst werden. Man kann auch Glasscherben zu Pulver vermahlen, Titanpulver und Kohlenstoffpulver z.B. Lampenruß zumischen und zusammenschmelzen, wobei für die Nitridbildung

Stickstoff aus der Luft entnommen wird. Die zwischen dem Metall und der Glasschmelze sich abspielenden metallurgischen Vorgänge führen offenbar zu anderen Produkten wie in den üblichen chemischen Methoden der Darstellung von Titan-nitrid und Titancarbid; denn die Zugabe der chemisch hergestellten Verbindungen zu den Glasschmelzen führt nicht zu dem gewünschten Erfolg. Diese führt vielmehr zu starker grobblasiger Schaumbildung unter Zersetzung der Verbindungen und unter Bildung dreiwertiger Oxide des Titans.

An Stelle von Titan können auch andere Metalle der 4. bis 6. Nebengruppe des Periodensystems verwendet werden, wobei für Herstellung trivalenter, stickstoffhaltiger Gläser die Metalle Titan, Niob und Tantal und für die Herstellung tetravalenter Gläser die Metalle Vanadin, Molybdän und Wolfram zu bevorzugen sind. Titan verhält sich in allen Fällen optimal, sowohl für die Nitridbildung wie für die Carbidbildung. Von besonderem Vorteil ist die Anwesenheit der Oxide des Eisens und des Mangans in der Schmelze, die offenbar die Löslichkeit der Reaktionsprodukte in der Glasschmelze erhöhen. Es sind für die Darstellung praktisch alle technischen Gläser geeignet, auch die Silikatschmelzen der Gesteine. Die erfindungsgemäßen Gläser sind Mischgläser der beiden Klassen von divalenten und trivalenten bzw. von divalenten und tetravalenten oder von di-, tri- und tetravalenten Gläsern, in denen die Nitride und Carbide des Titans bzw. der anderen Metalle als komplexe Verbindungen, in denen meist Eisen oder ein anderes Metall enthalten ist, vorliegen.

Besonders auffallend ist die hohe Härte der erfindungsgemäßen Gläser, mit denen sich normale Gläser leicht schneiden lassen. Die Härte entspricht der von Hartmetallen, So liegen auch die Brechungsindizes höher als bei divalenten Gläsern.

Von großem technischen Interesse ist geschäumtes, zelluläres tri- und tetravalentes Glas für Dichtungen, Isolationen, Filtermaterial, Katalysatorträger und dergl. Es bildet sich aus den Schmelzen bei Überschuß der flüchtigen Bestandteile wie  $N_2$ , CO und  $CO_2$ .

## 3

Die Mischungsverhältnisse der tri- und tetravalenten Gläser mit den divalenten Gläsern können in weiten Grenzen liegen, sowohl Mischgläser mit kleinen Anteilen von divalenten Gläsern, wie auch Mischgläser mit großen Anteilen divalenter Gläser sind herstellbar. Die Löslichkeit unter einander ist lückenlos.

Beispiel 1

Man pulverisiert Scherben von Fensterglas soweit, daß sie bis zu 55 % Korngrößen unter 0,075 mm haben, mischt 5 % Titanpulver unter 20 $\mu$  dazu, erhitzt bei Pulverschichtdicken von 25 mm und mehr auf 875°C, wobei das Titan unter Stickstoffaufnahme aus der Luft von der Glasschmelze vollständig unter Bildung eines bronzefarbenen Mischglases gelöst wird. Man erhält so ein geschäumtes zelluläres Produkt, das bei weiterer Temperaturerhöhung zu einem blasenfreien Glas geläutert werden kann.

Beispiel 2

Man mischt zu Glaspulver aus Fensterglas in der Kugelmühle 5 % Titanpulver und 1 % Lampenruß und erhitzt auf 875°C. Es wird ein Produkt von tiefschwarzer Farbe, hohen Glanz und außerordentlicher Härte erhalten, mit dem man Fensterglas schneiden kann. Es läßt sich ebenfalls bei erhöhter Temperatur läutern. Ungeläutert und mit Überschuß von Ruß liegt es als Schaumglas vor.

Beispiel 3

Für die Herstellung eines Plättchens von hoher Härte zur Metallbearbeitung mischt man Titanpulver und Glaspulver im Gew.-Verhältnis 1:1 und füllt damit eine kleine Kastenform entsprechender Abmessungen und erhitzt auf 875°C. Man erhält ein hartes, bläschenfreies Plättchen, dessen Härte durch Zumischen von Lampenruß erhöht werden kann.

Alle Produkte nach Beispiel 1 bis 3 müssen im Glasentspannungsofen bei 500°C entspannt werden.

P a t e n t a n s p r ü c h e

1. Verfahren zur Herstellung von tri- und tetravalenten Gläsern, dadurch gekennzeichnet, daß Titanmetallpulver in Glasschmelzen von Normalglas eingeführt und mit den in der Schmelze vorhandenen und oder zugegebenen Reaktionsteilnehmern Stickstoff und oder Kohlenstoff, vorzugsweise in Form seiner Oxide CO und CO<sub>2</sub>, zu Reaktionsprodukten umgesetzt wird, die in der Glasschmelze löslich sind.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß an Stelle von Titan die Metalle der 4. bis 6. Nebengruppe des Periodensystems der Elemente verwendet werden.
3. Verfahren nach Anspruch 1 und 2, dadurch gekennzeichnet, daß an Stelle von Normalglas technische Gläser mit mehr oder weniger weitgehenden Änderungen in der Zusammensetzung des Normalglases, vorzugsweise mit einem Gehalt an Oxiden des Eisens und Mangans, oder borat- und phosphathaltige Gläser verwendet werden.
4. Verfahren nach Anspruch 1 und 2, dadurch gekennzeichnet, daß an Stelle der Schmelzen von Normalglas Schmelzen silikatischer Gesteine und Mineralien verwendet werden.
5. Verfahren nach Anspruch 1 bis 4, dadurch gekennzeichnet, daß Glasscherben zu Pulver gemahlen, mit Metallpulver vermischt und zusammengeschmolzen werden.
6. Verfahren nach Anspruch 1 bis 4, dadurch gekennzeichnet, daß Glasscherben zu Pulver gemahlen, mit Metall- und Kohlenstoffpulver, vorzugsweise in Form von Lampenruß, vermischt und zusammengeschmolzen werden.
7. Verfahren nach Anspruch 1 bis 6, dadurch gekennzeichnet, daß die Glasschmelzen durch einen Überschuß der flüchtigen Bestandteile zum Schäumen gebracht werden.



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(54) Coated refractory article and method.

(57) For protection against oxidation or other adverse chemical deterioration, substrates such as carbon, intermetallic aluminides, and refractory metal alloys are provided with barrier coatings of an aluminoborate glass-ceramic coating having a composition, in weight percent, of about 10-55%  $\text{Al}_2\text{O}_3$ , 4-40%  $\text{B}_2\text{O}_3$ , up to 70% total of RO, wherein RO consists of one or more alkaline earth metal oxides selected in amounts not exceeding the indicated proportions from the group consisting of up to 70% BaO, up to 60% SrO, up to 40% CaO, and up to 25% MgO, up to 35% total of  $\text{R}_2\text{O}$ , wherein  $\text{R}_2\text{O}$  consists of one or more alkali metal oxides selected in amounts not exceeding the indicated proportion from the group consisting of up to 35%  $\text{Na}_2\text{O}$ , up to 30%  $\text{K}_2\text{O}$ , and up to 15%  $\text{Li}_2\text{O}$ , up to 25% total of metal oxides selected from the group consisting of ZnO and MnO, up to 30% of  $\text{SiO}_2$ , and up to 10% F.

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Background of the Invention

The present invention relates to protective glass-ceramic coatings and to refractory structural articles provided with the protective coatings. More specifically, the invention pertains to glass-ceramic coatings useful for the protection of oxidizable refractory substrate materials such as refractory intermetallic aluminides, titanium alloys, carbon-carbon composites, and iron, cobalt or nickel-based superalloys. The coatings provide a chemical barrier which is effective to protect the substrate from oxidation or other physical or chemical deterioration at high temperatures in hostile environments.

There is a continuing need for materials offering good strength and toughness as well as excellent resistance to chemical attack at very high use temperatures. In the aerospace industry, for example, refractory materials such as carbon-carbon composites, superalloys, and intermetallic titanium aluminide compounds are being increasingly used for airframe, engine and other components for supersonic and advanced ultrasonic aircraft such as the national aerospace plane (NASP).

Aluminide intermetallic compounds, which are candidates for large structural components of the space plane, offer a unique combination of low density, high strength, and sustained resistance to temperatures up to 1000 °C. However, each of the two aluminide candidate materials presently being evaluated, i.e., titanium aluminide in the gamma form (TiAl) and in the super  $\alpha$ -2 form (Ti<sub>3</sub>Al), are susceptible to oxidation attack as well as to hydrogen embrittlement at elevated temperatures.

Carbon is one of the most refractory elements known, with a melting point of over 4000 °C, and new composite materials composed of carbon reinforced with carbon fibers offer the highest strength/weight ratios of any known materials. Unfortunately, the reactivity of carbon with oxygen to form CO<sub>2</sub> at temperatures below about 600 °C severely limits the usefulness of carbon-based materials in oxidizing environments. The promise of a carbon-carbon composite that could be protected from oxidation to make full use of its high strength/weight ratio and melting point has attracted great interest in the aerospace community.

Protective coatings of silicon carbide, applied by various techniques such as direct solid-state reaction, sputtering, evaporation, or the like, are known to provide limited protection to carbon composite materials at temperatures in the 1000 °C range, but cracking and oxidation remain persistent problems. Boron oxide, alone or in combination with other oxides, has been incorporated in the these substrates and/or the coatings to improve crack resistance, but the resulting materials characteristically melt at low temperatures and lose their effectiveness at temperatures much above 1000 °C.

Also benefitting from protective coatings are metallic components composed of the so-called superalloys. These alloys are typically iron-, nickel- or cobalt-based alloys comprising substantial proportions of chromium, iron, cobalt or nickel as alloying constituents. Although more oxidation-resistant than carbon composite materials, these alloys are also subject to high temperature oxidation, and therefore have also been protectively coated for increased high-temperature protection.

A conventional method for protecting refractory materials such as described from oxidation at elevated temperatures is to apply a continuous monolithic glass coating thereto. Glass can completely encapsulate and isolate a protected substrate from the surrounding atmosphere; however, glass layers are subject to erosion or displacement by viscous flow at high temperatures.

The high temperature viscosity of glass coatings may be increased by mixing crystalline materials with the glass frits before application of the coating. However, these glass-crystalline mixtures sinter non-uniformly, and the crystal size, homogeneity, and flow of the coatings are thus very difficult to control.

Polycrystalline ceramic coatings have been proposed as a way to protect superalloy materials from oxidative deterioration. Thus U.S. Patents Nos. 4,485,151 and 4,535,033 (Stecura) describe the application of insulating layers of stabilized ZrO<sub>2</sub> to such materials via a plasma-spraying technique.

Ceramic plasma spraying procedures can involve several steps that are tedious and difficult to control in commercial production. Further, thermal gradients tend to develop during plasma-spraying which introduce defects in the finished coating, and the finished coatings tend to be porous. This permits access of gases, in particular O<sub>2</sub>, H<sub>2</sub>, SO<sub>2</sub>, and water vapor, all of which can contribute to coating failure.

Glass-ceramic materials are of course well known and a wide variety of glass-ceramic compositions for various uses, including coatings, has been developed. U.S. Patent No. 3,397,076 (Little et al.), for example, describes fused crystallizable ground and cover coats for high temperature alloys in which the major elements are cobalt, nickel, chromium, iron or mixtures. The ground coat is lithium-free and contains 35-65% SiO<sub>2</sub> and 12-45% BaO. Examples also contain substantial amounts of R<sub>2</sub>O, B<sub>2</sub>O<sub>3</sub> and/or TiO<sub>2</sub>.

U.S. Patent No. 3,467,534 (MacDowell) discloses glass-ceramic articles consisting essentially of 20-70% BaO and 30-80% SiO<sub>2</sub> and having a barium silicate principal crystal phase. A preferred example is described as considered for coating metals. U.S. Patent No. 4,861,734 (MacDowell) discloses alkaline earth



aluminoborate glass-ceramics, produced through a process of sintering finely-divided borate glasses of appropriate composition, which exhibit relatively high levels of crystallinity and dielectric properties rendering them suitable for applications such as integrated circuit packaging.

Notwithstanding the fact that both glass-ceramic and glass coating technologies are highly developed, there remains a need for new protective coating formulations which could protect refractory carbonaceous, metallic, and intermetallic surfaces from oxidation or other deterioration at high temperatures. It is accordingly a principal object of the present invention to provide protective coatings of improved integrity and refractoriness for use in the protection of such substrates.

Another object is to provide such coatings which are both more effective than previously known coatings and more convenient to apply.

A further object is to provide protective coatings which are non-porous, continuous and free from defects such as pinholes and cracks, and thus a barrier to the diffusion of oxygen as well as hydrogen and other corrosive gases.

A still further object is to provide a barrier coating that adheres tightly to various refractory substrates and resists spalling during thermal cycling.

Another object is to provide an oxygen barrier coating material that exhibits the excellent flow characteristics of a glass coating as it is fired in one temperature range, and becomes resistant to flow (due to crystallization) as it is heated in a higher temperature range.

A further object is to provide a protectively coated article comprising a substrate portion composed of a carbon composite, intermetallic or metal alloy and a protective glass-ceramic coating offering improved resistance to mechanical abrasion and chemical corrosion, adherence, refractoriness, integrity and/or permeation resistance than prior art coatings.

#### Summary of the Invention

We have now identified a family of aluminoborate glasses which provide excellent flow, good substrate coverage, desirable crystallization behavior, and a crystallized glass-ceramic coating of high density and low permeability for the protection of refractory substrates. The glass-ceramic coatings can be selected to provide excellent integrity and adherence to oxidizable refractory inorganic substrates, including substrates such as the intermetallic aluminides, metal alloys, and carbon-based materials such as carbon composites. Examples of particular substrates include carbon-fiber-reinforced carbon matrix composites, titanium aluminides, titanium alloys, and nickel-based, iron-based, and cobalt-based superalloys.

A primary concern with respect to borate-based glass-ceramics relates to the relatively large proportions of  $B_2O_3$  present, and to the resulting residual low-melting glass phases expected in crystallized articles produced from such compositions. Hence borate glass-ceramics are not attractive candidates for high-temperature applications, since the estimated maximum use temperatures were far below the 1000 °C capabilities thought to be required to achieve significant improvements in refractory substrate protection.

Surprisingly, the present invention includes aluminoborate glass-ceramic compositions that can form smooth, adherent, spall-free coatings capable of withstanding temperatures of 1000 °C and higher for prolonged periods. Also included are compositions providing coatings offering improved flow, adherence and other properties at temperatures below 1000 °C. Further, refractory aluminoborate coatings within the composition range of the invention can be formulated for compatibility with a number of refractory substrates, including, for example, carbon-carbon composites, iron, nickel, and cobalt-based superalloys, and titanium aluminides.

The invention thus comprises, in broad aspect, a refractory substrate material composed of a carbon, aluminide or metallic alloy material as above described upon which is provided at least one surface barrier layer comprising or consisting of a protective aluminoborate glass-ceramic coating. Aluminoborate glass compositions useful for the application of glass-ceramic coatings in accordance with the invention will consist essentially, in weight percent, of about 10-55%  $Al_2O_3$ , 4-40%  $B_2O_3$ , up to 70% total of RO, wherein RO consists of one or more alkaline earth metal oxides selected in amounts not exceeding the indicated proportions from the group consisting of up to 70% BaO, up to 60% SrO, up to 40% CaO, and up to 25% MgO, up to 35% total of  $R_2O$ , wherein  $R_2O$  consists of one or more alkali metal oxides selected in the indicated proportion from the group consisting of up to 35%  $Na_2O$ , up to 30%  $K_2O$ , and up to 15%  $Li_2O$ , up to 25% total of metal oxides selected from the group consisting of ZnO and MnO, up to 30% of  $SiO_2$ , and up to 10% F.

In another aspect, the invention comprises a method for the protection of a refractory substrate from oxidation or other chemical attack. That method comprises the steps of applying a glass coating directly or indirectly to the substrate, and thereafter heating the glass coating, typically by heating the glass and

substrate, to promote crystallization (thermal curing) of the glass coating. In a preferred embodiment, the glass coating is applied to the substrate as a glass powder. The method of the invention provides a continuous protective crystalline or semicrystalline glass-ceramic coating on the substrate.

Glass compositions within the above described composition region can be melted and converted to glass powders by conventional glass processing methods, and can be applied in powder form to selected refractory substrates to produce coatings of any selected thickness. Powder coatings thus provided can then be sintered as glasses, typically at temperatures well below 900 °C, and thereafter crystallized by firing under an appropriate atmosphere at temperatures in the range of about 900-1100 °C. The resulting glass-ceramic coatings will generally be highly crystalline, dense and continuous, as well as spall- and crack-resistant on substrates of appropriate chemical reactivity and thermal expansion characteristics.

The present coatings offer significant and unexpected advantages over prior art coatings, not only with respect to reduced curing temperatures, but also in terms of coating behavior. Because crystallization in these coatings tends to be somewhat delayed in comparison with prior art silicate coatings, flow during curing is more extensive, and better coating coverage can be achieved. In addition, typical concentrations of residual glass are high enough to impart a self-healing quality to the coatings, yet the glass-crystalline mixture is sufficiently hard or refractory overall that the service temperature of the coatings is not unduly compromised.

In many cases, the protective glass-ceramic coatings of the invention will be used in combination with other coatings to provide a fuller range of substrate protection and performance. In the case of carbon-carbon composites, for example, a primer or base coating of silicon carbide or a similar material is highly desirable in order to provide a substrate or foundation for overcoating with aluminoborate glass-ceramic coatings of the invention. In other cases, semi-crystalline or crystalline overcoatings may be used in combination with the glass-ceramic coatings of the invention to provide a coating system of particularly high refractoriness and durability.

#### Detailed Description

An important performance characteristic of any glass-ceramic coating system is an appropriate balance between adequate viscous flow and densification of the glass during the early firing stages and crystallization of the coating prior to completion of the firing cycle. Premature crystallization results in insufficient flow and a rough, porous coating, whereas insufficient crystallization results in excess quantities of residual glass and thus a less refractory coating. The present compositions generally achieve excellent balance between early stage viscous flow and high cured crystallinity.

Also important is the thermal expansion match between the coating and the substrate. Although in some instances the expansion of the coating will be modified by interaction with the substrate during curing, carbon substrates will generally require coatings of relatively low thermal expansion while metal alloys and intermetallic aluminides will require relatively high expansion coatings. Again, the coatings of the invention can be adjusted for thermal expansion, and can provide final coatings which are well matched to either type of substrate in terms of physical properties.

As previously noted, the preparation of glass powders from the aluminoborate glasses utilized to form the coatings can follow conventional practice. The glasses are compounded of conventional glass batch constituents, typically oxides of the selected metals, and then mixed and melted at temperatures typically in the range of 1500-1700 °C to provide homogeneous fluid melts. The melts are then converted into granular glass by drigaging or other fritting method, and the granular pre-product is then milled to provide fine glass powder. The preferred particle sizes of the milled glass are typically in the 5-20 micron range, although smaller particle sizes may be preferred where very thin coatings are required.

The surface of a selected refractory substrate to be protected may be coated with the powdered glass in any conventional manner. The presently preferred method is electrostatic spraying, wherein electrostatically-charged, dry glass powder is sprayed with a high degree of uniformity onto the surface of the selected substrate while the latter is supported on an oppositely charged wire mesh screen. Alternatively, the powdered glass may be mixed with a suitable medium, e.g., water or an organic vehicle, applied uniformly over the surface of the substrate, and dried.

The glass powder-coated substrate is then typically heated to a temperature in the range of 800-1100 °C. At these temperatures, the glass particles initially soften and flow to produce a dense, smooth, well-formed continuous glass coating that is essentially free from crystallization. Further heating, within the same or a higher temperature range, is effective to initiate and then complete the development of crystal phases to form a dense, strong, refractory, crystalline or semicrystalline coating.

The invention may be further illustrated by specific examples of aluminoborate glass-ceramic coating

compositions useful in accordance with the invention as set forth in Table I below. The compositions are reported on a parts by weight basis, but closely approximate weight percent. These formulations, which are particularly suitable for use for the protection of aluminide intermetallic and/or metal alloy substrates, can yield smooth, non-porous coatings that adhere well to these substrates.

Table I

Aluminoborate Glass-Ceramic Coating Compositions

	Sample		Oxide						
	No.	BaO	SrO	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Other
10	1	56.0	-	-	-	18.6	25.4	-	-
15	2	50.4	-	-	-	16.8	22.9	9.9	-
	3	57.0	-	-	-	18.9	12.9	11.1	-
	4	55.4	-	-	-	12.3	25.1	7.2	-
20	5	66.5	-	-	-	14.7	10.1	8.7	-
	6	61.2	-	-	-	13.6	9.3	16.0	-
	7	-	54.7	-	-	26.9	18.4	-	-
25	8	-	47.2	-	-	23.2	15.9	13.7	-
	9	-	57.3	-	-	18.8	12.8	11.1	-
	10	-	-	32.6	-	29.7	20.2	17.5	-
30	11	-	-	35.8	-	32.5	22.2	9.6	-
	12	42.0	-	-	11.0	27.9	19.1	-	-
	13	38.8	-	-	10.2	25.8	17.6	7.6	-
35	14	35.3	-	-	9.3	23.5	32.0	-	-
	15	28.6	-	-	7.5	38.0	25.9	-	-
	16	32.9	-	-	17.3	21.9	15.0	12.9	-
40	17	-	-	-	10.7	27.1	37.1	-	25.1 K <sub>2</sub> O
	18	38.7	-	-	-	25.8	17.6	-	17.9 MnO
	19	37.7	-	-	-	25.1	17.1	-	20.0 ZnO
45	20	-	19.6	-	-	38.6	26.4	-	15.4 ZnO
	21	26.0	-	-	-	34.5	23.6	-	15.9 K <sub>2</sub> O
	22	-	-	-	9.1	45.8	31.2	-	13.9 Na <sub>2</sub> O
50	23	-	-	-	-	41.9	28.6	-	12.7 Na <sub>2</sub> O 16.7 ZnO
	24	-	-	25.2	-	45.8	15.6	13.4	-
	25	-	21.0	11.4	-	41.4	14.1	12.2	-
55	26	28.3	-	10.3	-	37.6	12.8	11.0	-
	27	30.5	-	11.0	-	40.1	6.8	11.8	-
	28	-	-	23.8	-	43.3	7.4	25.5	-
	29	-	-	22.0	-	53.3	9.1	15.7	-

Table I (continued)

Sample	Oxide								
	No.	BaO	SrO	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Other
5	30	-	23.9	12.9	-	47.1	16.1	-	-
	31	31.8	-	11.6	-	42.2	14.4	-	-
10	32	56.0	-	-	-	18.6	25.4	-	6.0 F
	33	66.5	-	-	-	14.7	10.1	8.7	-
	34	-	-	28.4	-	38.8	17.6	15.2	-
15	35	52.9	-	-	-	35.2	12.0	-	-
	36	47.9	-	-	-	31.9	10.9	9.4	-
	37	17.8	12.0	6.5	-	39.0	13.3	11.5	-
	38	-	40.9	-	-	40.3	6.9	11.9	-
20	39	50.6	-	-	-	33.7	5.7	9.9	-
	40	27.6	18.6	-	-	36.7	6.3	10.8	-
	41	-	36.6	-	-	36.0	6.1	21.2	-
25	42	-	-	28.4	-	38.8	17.6	15.2	-

To prepare glass powders from the compositions reported in Table I, glass batches of corresponding oxide composition are mixed and melted in platinum crucibles at about 1600 °C for two hours. The glass melts thus obtained are then poured into water to quench and granulate the glass. The granular glass (drillage) is thereafter ball milled with alumina cylinders for 4 to 8 hours to provide powdered glass with an average particle size of about 10 micrometers.

The crystallization behavior of glasses of the above composition is evaluated by dry pressing the powdered glasses into cylinders 1/2" in diameter and heat-treating the cylinders at temperatures of 800-1200 °C for 1/2-1 hour to determine their sintering characteristics. To determine the thermal expansion coefficients and densities (porosities) of the glass-ceramic products, 4"x1/4"x1/4" bars are pressed from the powdered glass, sintered, and crystallized to glass-ceramics.

In many cases X-ray diffraction analyses are conducted on fired samples to determine crystal phases developed during firing. In general these analyses reveal alkaline earth aluminate or aluminoborate phases or, if silica is present, alkaline earth aluminosilicate phases.

Coatings of the compositions shown in Table I are also applied to aluminide or metal alloy coupons to confirm the compatibility of the glass and glass-ceramic coating materials with these particular substrates. The specific substrate materials tested include gamma-titanium aluminide (TiAl), super alpha-2 titanium aluminide (Ti<sub>3</sub>Al), and Inconel 718 alloy.

The coatings are applied in thicknesses between 20 and 100 micrometers to coupons of 2 mm thickness using electrostatic spraying. The surfaces of the coupons are cleaned and grit-blasted prior to coating. Each glass-coated coupon is then fired at an appropriate peak temperature, typically 900, 1000, or 1100 °C, in an air or flowing helium (low-oxygen) atmosphere. The samples are placed in the firing furnace at ambient temperature, heated to the selected peak firing temperature at a furnace heating rate of approximately 75 °C per minute, and maintained at the peak firing temperature for about one hour.

Illustrative results from evaluations such as described above as conducted on Inconel 718 alloy substrates are reported in Table II below. The sample numbers in Tables I and II correspond for cross reference. Included in Table II for each of the Table I compositions tested are the peak heat treatment temperature, glass-ceramic density, and thermal coefficient of expansion (TCE) data as determined on pressed crystallized bars, and crystal phase descriptions where determined on individual samples. Also included are descriptions of the appearance of each glass-ceramic coating on the alloy substrates. Most of the firings onto alloy substrates were conducted in a low oxygen (flowing helium) atmosphere to prevent excessive oxidation prior to coating consolidation.

The expansion coefficients and densities given in Table II are those obtained on pressed and fired bars. As previously noted, reaction of the coating with the oxide surface of the substrate during firing will substantially alter the composition of the coating in the interfacial region, altering the thermal expansion and density of the coating in that region as well.

- 5 As the coating descriptions indicate, small seed and pinhole defects are observed in some of the coatings, particularly if very thin, but no spalling of the coatings is observed. The pinhole defects may of course be avoided by better sample preparation and/or the use of thicker coatings.

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Table II

Aluminoborate Glass-Ceramic Coatings  
on Alloy Substrates

Sample No.	Heat Treatment (1 hr. in He) /	TCE	Density	Phases
	Appearance			
1	900° very smooth/glossy dark grey-green	86.6	3.619	
2	900° slightly rippled semigloss grey	85.9	2.555	(BaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> )
3	900° semigloss dark grey opaque/rippled	93.0	3.627	BaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>
4	900° dark grey semigloss/ slightly dimpled			(BaB <sub>2</sub> O <sub>4</sub> )
4	1000° grey-green semigloss			
5	900° glossy dark grey opaque/rippled	102.5	4.070	
6	1000° semigloss/thin/ pinholes	97.3	3.779	BaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>
7	900° very dark grey-green/ glossy & smooth		3.432	SrAl <sub>2</sub> O <sub>4</sub>

Table II (continued)

Heat Treatment					
Sample	(1 hr. in He) /				
No.	Appearance	TCE	Density	Phases	
8	900° translucent/grey/ semigloss/few pinholes	75.1	3.188	SrAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	
9	900° dark grey opaque/ semigloss/rippled	86.9	3.556	Sr <sub>2</sub> Al <sub>2</sub> B <sub>2</sub> O <sub>7</sub>	
10	900° very smooth semigloss translucent grey	65.0	2.517	α-CaAl <sub>2</sub> B <sub>2</sub> O <sub>7</sub>	
11	900° thick/glossy/ translucent grey	55.7	2.255	α-Ca <sub>2</sub> Al <sub>2</sub> B <sub>2</sub> O <sub>7</sub>	
12	900° very smooth dark grey semigloss	90.3	3.554	MgAl <sub>2</sub> O <sub>4</sub>	
13	900° smooth glossy/light grey/some pinholes	74.2	3.255	BaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	
14	900° smooth/dull grey/ some pinholes	78.3	2.534	-	
15	900° blue-grey semigloss/ rippled surface	65.6	2.925	(mullite)	

Table II (concluded)

Heat Treatment					
Sample (1 hr. in He) /					
No.	Appearance	T.E.	Dens.	Phases	
16	900° grey glossy/slightly rippled/few pinholes	101.6	3.219	BaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	
17	900° white opaque thick/ glossy	107.4	2.253	MgAl <sub>2</sub> O <sub>4</sub>	
18	900° glossy/very fine blisters	87.7	3.428		
19	900° smooth grey semigloss	92.5	3.344	Ba <sub>8</sub> Al <sub>2</sub> O <sub>11</sub>	
20	900° glossy light blue/ slightly textured	62.2	2.631	ZnAl <sub>2</sub> O <sub>4</sub>	
21	1000° seedy/translucent/ lumpy	73.9			
22	1000° very hard/grey-brown/ surface blister	94.3		MgAl <sub>2</sub> O <sub>4</sub>	
23	1000° very hard/grey-brown/ surface blisters	91.4		ZnAl <sub>2</sub> O <sub>4</sub>	



Table II (continued)

Sample No.	Heat Treatment (1 hr. in He)	TCE	Density	Phases
	Appearance			
24	1000° rough/translucent/ lumpy/hard	71.2	2.463	$\text{CaAl}_2\text{Si}_2\text{O}_8$
25	1000° rough/translucent/ lumpy/hard	67.1	2.872	slawsonite
26	1000° hard/translucent/ pinholes	82.0	3.036	$(\text{Ba}, \text{Ca})\text{Al}_2\text{Si}_2\text{O}_8$ (Hex.)
27	1000° translucent/lumpy	80.5		
28	1000° transparent/translucent crystals/hard/smooth/ pinholes	63.1	2.741	$\text{CaAl}_2\text{Si}_2\text{O}_8$
29	1000° clear/hard/transparent and translucent/ few pinholes	69.4	2.767	$\text{CaAl}_2\text{Si}_2\text{O}_8$

Evaluations similar to those conducted on metal alloy substrates were also conducted on titanium aluminide substrates. The coating procedures followed were similar to the procedures utilized to apply the coatings to alloys as described above. In general, however, firing of the coatings onto  $\text{Ti}_3\text{Al}$  substrates was carried out in air, while the coatings on  $\text{TiAl}$  were carried out in a low-oxygen atmosphere (flowing helium).

Table III below reports the results of a number of coating evaluations on titanium aluminides. Included in Table III for each of the coatings tested are an identification of the substrate (Subs.) composition, a report of the heat treatment atmosphere and peak temperature used, and the appearance of the fired coating. Again, the Sample numbers used in Table III correlate with the original Sample numbers defined in Table I above. Also included in Table III are the thermal expansion coefficients, densities, and crystal phases present in the coatings, where determined on individual samples.

Table III

Aluminoborate Glass-Ceramic Coatings  
on Ti-Al Substrates

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	<u>No.</u>	<u>Subs.</u>	<u>Heat</u>	<u>Appearance</u>
			<u>Treatment</u> <u>(°C/1 hr)</u>	
10	11	Ti <sub>3</sub> Al	900/Air	thin/flat/finely textured black
	12	Ti <sub>3</sub> Al	900/Air	transparent/very fine seed
	15	TiAl	900/He	smooth/translucent grey/few pinholes
15	17	Ti <sub>3</sub> Al	900/Air	clear transparent/white crystals
	19	Ti <sub>3</sub> Al	900/Air	glossy grey/some pinholes
	25	TiAl	1000/He	hard/smooth/translucent/few pinholes
	25	TiAl	1100/He	rough translucent/white & yellow
20	26	TiAl	1000/He	smooth transl./small blisters-pinholes
	27	TiAl	1000/He	hard/thin/rough texture
	28	TiAl	1000/He	hard/rough/transl. grey/white crystals
25	30	TiAl	1000/He	transparent-translucent crystals/hard
	31	TiAl	1000/He	transparent-translucent crystals/hard
	32	Ti <sub>3</sub> Al	900/Air	very thin glassy/"puddling" of excess
30	32	TiAl	900/He	very smooth transparent/appears black
	33	Ti <sub>3</sub> Al	900/Air	smooth/transparent/appears black
	35	TiAl	1100/He	hard/rough grey translucent
	36	TiAl	1000/He	smooth transparent/slightly seedy
35	37	TiAl	1000/He	seedy/transparent-translucent/ fine blisters
	38	TiAl	1000/He	very thin/rough/transparent
40	39	TiAl	1000/He	thin/rough/transparent
	40	TiAl	1000/He	hard/thin/rough texture
	41	TiAl	1000/He	transparent-translucent/rough texture
	42	TiAl	900/He	very smooth grey/transparent/fine seed

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Table III cont'd

Aluminoborate Glass-Ceramic Coatings  
on Ti-Al Substrates

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	Sample No.	Thermal Expansion ( $\times 10^{-6}/^{\circ}\text{C}$ )	Density (g/cc)	Phases Present (XRD)
10	11	55.7	2.255	$\alpha\text{-CaAl}_2\text{B}_2\text{O}_7$
	12	90.3	3.554	$\text{MgAl}_2\text{O}_4$
	15	65.6	2.925	mullite
15	17	107.4	2.253	$\text{MgAl}_2\text{O}_4$
	19	85.7	2.994	$\text{ZnAl}_2\text{O}_4$
	25	67.1	2.872	-
	25-(1100 $^{\circ}\text{C}$ )	67.2	-	-
20	26	82.0	3.036	$(\text{Ba}, \text{Ca})\text{Al}_2\text{Si}_2\text{O}_8 (\text{Hex.})$
	27	80.5	3.073	-
	28	63.1	2.714	$\text{CaAl}_2\text{Si}_2\text{O}_8$
25	30	51.7	2.934	-
	31	83.2	3.296	-
	32-( $\text{Ti}_3\text{Al}$ )	86.6	3.619	-
30	33	102.5	4.070	-
	35	85.8	3.121	-
	36	-	3.364	$\text{BaAl}_2\text{Si}_2\text{O}_8 (\text{Hex.})$
35	37	54.6	2.967	$(\text{Ba}, \text{Sr}, \text{Ca})\text{Al}_2\text{Si}_2\text{O}_8 (\text{Hex.})$
	38	67.7	3.173	-
	39	69.6	3.521	-
	40	75.9	3.285	-
40	41	54.3	3.069	$\text{CaAl}_2\text{Si}_2\text{O}_8$
	42	64.0	2.669	-

45 Specific examples of aluminoborate glass-ceramic coating compositions which are particularly useful in accordance with the invention for the protection of carbon-carbon composite substrates are set forth in Table IV below. The compositions in Table IV are again reported on a parts by weight basis in approximate weight percent.

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Table IV

Aluminoborate Glass-Ceramic Coating  
Compositions for C-C Composites

No.	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MgO	CaO	SrO	BaO	Other
43	25.3	37.1	-	-	-	37.6	-	-
44	23.2	34.0	-	-	-	17.3	25.6	-
45	28.6	41.9	-	8.3	-	21.3	-	-
46	31.7	46.4	-	9.1	12.7	-	-	-
47	17.6	51.6	-	-	7.1	-	-	23.6 Na <sub>2</sub> O
48	17.8	52.1	-	-	14.3	-	-	15.8 Na <sub>2</sub> O
49	13.7	50.1	11.8	-	-	-	-	24.4 Na <sub>2</sub> O
50	17.7	51.8	15.2	-	-	-	-	15.2 Li <sub>2</sub> O
51	17.5	51.3	-	-	-	-	-	31.2 Na <sub>2</sub> O
52	12.0	35.2	-	-	-	-	52.8	-
53	13.1	38.4	-	-	-	19.5	28.9	-
54	10.1	29.5	-	-	16.2	-	44.3	-
55	10.8	31.7	-	-	-	32.2	-	25.3 ZnO
56	14.5	42.4	-	-	-	43.1	-	-
57	12.9	37.7	11.1	-	-	38.3	-	-
58	7.4	43.3	25.5	-	23.8	-	-	-
59	15.8	46.2	-	-	38.1	-	-	-
60	11.9	34.9	-	-	-	53.2	-	-
61	9.5	27.8	-	-	-	-	62.7	-
62	4.0	26.9	7.9	-	-	-	60.6	-
63	5.2	30.5	17.9	-	-	46.4	-	-

Glass powders having the compositions reported in Table IV can be prepared in the same manner as described above for the aluminoborate glass-ceramics reported in Table I. Again, the crystallization behavior of the glasses is evaluated from dry-pressed pellets crystallized at 800-1200 °C, and expansion and density data are determined from the pellets and/or glass-ceramic bars prepared by pressing, sintering and crystallizing the powders.

As with the previous aluminoborate formulations, the coating compositions in Table IV will provide dense glass-ceramic coatings when applied as powdered glass layers to carbon composite surfaces. However, our data clearly indicate a need to use an adherent base coating as a support and bonding medium for the protective aluminoborate glass-ceramic layer. The base coating will most preferably consist of a metal carbide that can develop a strong bond between the carbon-carbon composite material and the aluminoborate glass-ceramic overcoat. A particular illustrative example of such a coating is silicon carbide.

Coatings of the compositions shown in Table IV above, as well as additional coatings having compositions selected from Table I, are applied to coupons of carbon-carbon composite material to evaluate coating quality and adherence. The coupons were in each case provided with solid state reacted silicon carbide primer coats to insure good adherence of the protective aluminoborate glass-ceramic coatings.

The glass-ceramic coatings were applied in thicknesses of 20-200 micrometers to coupons of 2 mm thickness using electrostatic spraying. Each glass-coated coupon is then fired at a peak temperature of 900

to 1100 °C in a low-oxygen atmosphere (typically flowing helium). Again, the samples are placed in the firing furnace at ambient temperature, heated to the selected peak firing temperature at a furnace heating rate of approximately 75 °C per minute, and maintained at the peak firing temperature for about one hour.

Coating results obtained from the described testing procedure are reported below in Table V. The  
5 Sample numbers reported in Table V correspond to the Sample numbers for the coating compositions reported in Tables I and IV.

Included in Table V for each of the coatings tested are the peak heat treatment temperature used and the resulting appearance of the glass-ceramic coating. The resulting transparency of each coating is also reported. For selected samples, thermal expansion coefficient (TCE) data were generated as well.

10 As the coating descriptions indicate, some blister and pinhole defects are observed in some of the coatings, but no spalling of the coatings is observed. The pinhole defects may of course be avoided by better sample preparation and/or the use of thicker coatings. The complete absence of cracking in many of the examples is particularly surprising in view of the rather large difference in thermal expansion between some of the coatings and the carbon-carbon composite substrate used, the latter having an average TCE of  
15 about 30 ( $\times 10^{-7}/^{\circ}\text{C}$ ).

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Table V

Aluminoborate Glass-Ceramic Coatings on Carbon Substrates		
No.	Heat Treatment (°C for 1 hour) / Appearance	TCE (10 <sup>7</sup> /°C)
1	900 v. thin transparent/seed/no spalling or cracks	86.6
5	900 v. thin transparent/seed/no spalling or cracks	102.5
7	900 v. thin transparent coating/blisters/no spalling or cracks	-
12	900 cl. transparent/blisters/pinholes/no spalling or cracks	90.3
15	900 slt. transparent-translucent/crystals/pinholes/ no spalling or cracks	65.6
43	900 cl. transparent-translucent/smooth/no spalling or cracks	8.3
44	900 translucent/v. seedy/large voids/no spalling or cracks	-
44	1000 glossy/transparent/seedy	-

Table V (continued)

Sample No.	Heat Treatment (°C for 1 hour) / Appearance	TCE (10 <sup>1</sup> /°C)
45	900 translucent white/smooth/few pinholes/ no spalling or cracks	-
46	900 hazy translucent/pinholed/no spalling or cracks	-
47	1000 v. thin cl. transparent/white lumps/no spalling v. slt. cracking	94.5
48	1000 v. thin cl. transparent/hazy lumps/no spalling v. slt. cracking	74.7
49	1000 v. thin cl. transparent/cl. lumps/no spalling v. slt. cracking	137.4
50	1000 v. thin cl. transparent/blue-white lumps no spalling/v. slt. cracking	-
51	1000 v. thin glassy transparent with lumps & ridges/ no spalling or cracking	-

Table V (continued)

Sample No.	Heat Treatment (°C for 1 hour) / Appearance		XRD	TCE (10 <sup>7</sup> /°C)
5	52	1000 clear translucent, v. porous	BaAl <sub>2</sub> O <sub>4</sub>	84.0
10	52	1100 clear translucent, adherent, no cracks	BaAl <sub>2</sub> O <sub>4</sub>	84.0
15	53	1000 lt. cracking, clear, translucent, seedy	BaAl <sub>2</sub> O <sub>4</sub>	83.0
20	53	1100 translucent, fused, adherent, lt. cracks	BaAl <sub>2</sub> O <sub>4</sub>	-
25	54	1000 clear, transparent, thin, few v.f. cracks	-	-
30	55	1000 rough, clear, transparent, no cracks	-	-
35	56	1100 clear, transparent, filled SiC cracks	SrAl <sub>4</sub> O <sub>7</sub> (SrAl <sub>2</sub> B <sub>2</sub> O <sub>7</sub> )	73.7
40	57	1000 clear, transparent, seedy, ridges	β-SrAl <sub>2</sub> B <sub>2</sub> O <sub>7</sub>	51.4
45	58	1100 clear, transparent-translucent, lumpy	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	64.8
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Table V (continued)

Sample No.	Heat Treatment (°C for 1 hour) /	XRD	TCE (10 <sup>7</sup> /°C)
	Appearance		
59	1100 clear, transparent-translucent, seedy	CaAl <sub>4</sub> O <sub>7</sub>	-
60	1000 clear, transparent-translucent, v. thin, no cracks	SrAl <sub>2</sub> O <sub>4</sub>	89.4
60	1100 clear, rough, few seeds and voids, no cracks	-	-
61	1000 clear, transparent-translucent, v. thin, no cracks	BaAl <sub>2</sub> O <sub>4</sub>	-
62	1100 transparent, lumpy, few seeds, no cracks	BaAl <sub>2</sub> O <sub>4</sub>	-
63	1000 clear, transparent, seedy	SrAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	65.6

In some cases, aluminoborate coatings provided in accordance with the invention may comprise significant quantities of the alkali metal ions (K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>). Although these had been expected to cause some long-term instabilities in coatings designed for high-temperature use, sodium and lithium aluminoborates were surprisingly successful as coatings when fired at 1000 °C for one hour. In addition to good flow and adherence to the SiC undercoat, the alkali aluminoborate coatings showed little or no cracking after firing.

Nevertheless, for applications wherein high refractoriness is of particular importance, the preferred coatings in accordance with the invention will be those which are substantially free of the alkali metal oxides. In these cases, alkali-free compositions wherein the boron content is kept within the lower portion of the permissible range, i.e., in the range of about 4-25% B<sub>2</sub>O<sub>3</sub> by weight, will be particularly refractory.

It may also be useful for some applications to limit the level of silicate phase development, since such development can result in the formation of boron domains in the coating which tend to be of somewhat reduced chemical stability. For these purposes, silica-free compositions, or compositions containing not more than about 15% of silica by weight, are especially useful.

As previously noted, there are applications for refractory carbon composite, titanium aluminide and alloy components of the kind herein described which will require extended use above 1100 °C. Although perhaps not sufficient alone for long service at these temperatures, the aluminoborate glass-ceramic coatings of the invention are adaptable to such use if employed in combination with an overcoating of one or more

refractory ceramic materials. Examples of such overcoating materials might include cordierite ( $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ ), alkaline earth aluminosilicates, alpha-alumina,  $\text{ZrO}_2$ , or the like.

While the invention has been particularly described above with respect to specific materials and specific procedures, it will be recognized that those materials and procedures are presented for purposes of illustration only and are not intended to be limiting. Thus numerous modifications and variations upon the compositions and processes specifically described herein may be resorted to by those skilled in the art within the scope of the appended claims.

## Claims

1. An article of manufacture comprising a substrate formed of an oxidizable refractory inorganic material upon which is disposed at least one surface barrier layer, the surface barrier consisting essentially of an aluminoborate glass-ceramic coating having a composition, in weight percent, of about 10-55%  $\text{Al}_2\text{O}_3$ , 4-40%  $\text{B}_2\text{O}_3$ , up to 70% total of RO, wherein RO consists of one or more alkaline earth metal oxides selected in amounts not exceeding the indicated proportions from the group consisting of up to 70% BaO, up to 60% SrO, up to 40% CaO, and up to 25% MgO, up to 35% total of  $\text{R}_2\text{O}$ , wherein  $\text{R}_2\text{O}$  consists of one or more alkali metal oxides selected in amounts not exceeding the indicated proportion from the group consisting of up to 35%  $\text{Na}_2\text{O}$ , up to 30%  $\text{K}_2\text{O}$ , and up to 15%  $\text{Li}_2\text{O}$ , up to 25% total of metal oxides selected from the group consisting of ZnO and MnO, up to 30% of  $\text{SiO}_2$ , and up to 10% F.
2. An article in accordance with claim 1 wherein the surface barrier layer consists essentially of an aluminoborate glass-ceramic coating having a composition, in weight percent, of about 10-55%  $\text{Al}_2\text{O}_3$ , 4-40%  $\text{B}_2\text{O}_3$ , up to 70% total of RO, wherein RO consists of one or more alkaline earth metal oxides selected in amounts not exceeding the indicated proportions from the group consisting of up to 70% BaO, up to 60% SrO, up to 40% CaO, and up to 25% MgO, up to 25% total of metal oxides selected from the group consisting of ZnO and MnO, up to 10% F, said composition being essentially alkali-free.
3. An article in accordance with claim 2 wherein the glass ceramic coating has a  $\text{B}_2\text{O}_3$  content in the range of about 4-25% by weight.
4. An article in accordance with claim 3 wherein the glass ceramic coating has a  $\text{SiO}_2$  content not exceeding about 15% by weight.
5. An article in accordance with claim 1 wherein the substrate is selected from the group consisting of carbon, intermetallic aluminides, and refractory metal alloys.
6. An article in accordance with claim 5 wherein the substrate is an intermetallic titanium aluminide, or a titanium alloy, or a cobalt-based, nickel-based, or iron-based superalloy, or a carbon-fiber-reinforced carbon matrix composition, optionally provided with an adherent surface coating of silicon carbide.
7. An article in accordance with any one of claims 1-6 wherein the aluminoborate glass-ceramic coating is provided with a refractory ceramic overcoating.
8. An article in accordance with claim 7 wherein the refractory ceramic overcoating is selected from the group consisting of cordierite, alumina, zirconia, and refractory aluminosilicates.
9. A method for protecting an oxidizable refractory inorganic substrate material from chemical attack which comprises the steps of (i) applying a coating of an aluminoborate glass to the substrate and (ii) heating the glass coating to convert it to a protective crystalline or semicrystalline aluminoborate glass-ceramic coating, wherein the aluminoborate glass has a composition which consists essentially, in weight percent, of about 10-55%  $\text{Al}_2\text{O}_3$ , 4-40%  $\text{B}_2\text{O}_3$ , up to 70% total of RO, wherein RO consists of one or more alkaline earth metal oxides selected in amounts not exceeding the indicated proportions from the group consisting of up to 70% BaO, up to 60% SrO, up to 40% CaO, and up to 25% MgO, up to 35% total of  $\text{R}_2\text{O}$ , wherein  $\text{R}_2\text{O}$  consists of one or more alkali metal oxides selected in amounts not exceeding the indicated proportion from the group consisting of up to 35%  $\text{Na}_2\text{O}$ , up to 30%  $\text{K}_2\text{O}$ , and up to 15%  $\text{Li}_2\text{O}$ , up to 25% total of metal oxides selected from the group consisting of ZnO and

MnO, up to 30% of SiO<sub>2</sub>, and up to 10% F.

10. A method in accordance with claim 13 wherein the coating of aluminoborate glass is provided as a layer of glass powder.

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European  
Patent Office

## EUROPEAN SEARCH REPORT

Application Number

EP 91 10 9878

### DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 080 345 (CORNING GLASS WORKS) * page 4, last paragraph - page 5, paragraph 1 ** abstract, claims 1-10 *	1-3,5, 9-10	C 03 C 10/00 C 04 B 41/50 C 23 C 24/10 C 23 C 28/04
X	EP-A-0 080 344 (CORNING GLASS WORKS) * page 4, last paragraph - page 5, paragraph 1 ** abstract, claims 1-11 *	1-3,5, 9-10	
X	EP-A-0 043 705 (DANIEL DONCASTER & SONS LTD) * abstract, claims 1-8 *	1-3,5-6, 9-10	
A	GB-A-921 861 (COMPAGNIE DE SAINT-GOBAIN) * the whole document *	1-6,9-10	
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The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
Berlin		25 November 91	KUEHNE H C
<b>CATEGORY OF CITED DOCUMENTS</b> X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention  E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons  &: member of the same patent family, corresponding document			